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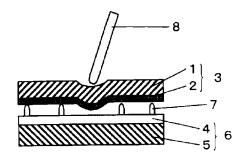
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# (54) 【発明の名称】透明導電膜付き化学強化ガラス基板、およびその製造方法

### (57)【要約】

【課題】透明導電膜の成膜条件下において強度低下が起 こらず、表面圧縮応力を維持できる透明導電膜付き化学 強化ガラス基板の提供。

【選択図】図1



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### 【特許請求の範囲】

#### 【請求項1】

がラス基板を化学強化することにより化学強化がラス基板が形成され、前記化学強化がラス基板上に透明導電膜が形成されてなる透明導電膜付き化学強化がラス基板であって、前記透明導電膜付き化学強化がラス基板は質量%表示で2~7%のNa2Oおよび0~3%のLi2Oを含有し、歪点が550℃以上であり、かつ表面圧縮応力が200~800MPaである透明導電膜付き化学強化がラス基板。

## 【請求項2】

前記透明導電膜付き化学強化ガラス基板は、厚さが 0 . 2 ~ 1 . 1 mmである請求項1 に記載の透明導電膜付き化学強化ガラス基板。

#### 【請求項3】

前記透明導電膜付き化学強化がラス基板は、質量%表示で4~13%のK2〇を含有する請求項1または2に記載の透明導電膜付き化学強化がラス基板。

#### 【請求項4】

前記透明導電膜付き化学強化ガラス基板は、質量%表示で45~70%の8iO2、2~20%のAI2O3、0~6%のB2O3、0~6%の区rO2 および10~25%のM9O+CaO+SrO+BaOをすらに含有する請求項3に記載の透明導電膜付き化学強化ガラス基板。

#### 【請求項5】

前記透明導電膜付き化学強化ガラス基板は、密度が2.4~2.6分/cm<sup>3</sup>である請求 20 項1~4のいずれが1項に記載の透明導電膜付き化学強化ガラス基板。

## 【請求項6】

前記透明導電膜付き化学強化ガラス基板は、圧縮応力層の深さが15~120μmである 請求項1~5のいずれか1項に記載の透明導電膜付き化学強化ガラス基板。

#### 【請求項7】

前記透明導電膜は、酸化スズ膜である請求項1~6のいずれか1項に記載の透明導電膜付き化学強化ガラス基板。

#### 【請求項8】

ガラス基板を化学強化することにより化学強化ガラス基板を形成し、前記化学強化ガラス 基板上に、常圧CVD法により透明導電膜を形成する透明導電膜付き化学強化ガラス基板の製造方法であって、

前記透明導電膜付き化学強化ガラス基板は、質量%表示で2~7%のNの2 O および0~3%のLi2 O を含有し、歪点が5 5 0 で以上であり、かつ表面圧縮応力が2 0 0~8 0 0 M P のであることを特徴とする透明導電膜付き化学強化ガラス基板の製造方法。

# 【発明の詳細な説明】

#### [0001]

#### 【発明の属する技術分野】

本発明は、特にタッチパネル用に適した、透明導電膜付き化学強化がラス基板、およびやの製造方法に関する。

# [0002]

【従来の技術】

がラス基板上に酸化スズ、酸化インジウムスズ(ITO)などの透明導電膜が形成された透明導電膜付きがラス基板は、タッチパネル、ディスプレイ、太陽電池用カパーがラス、帯電防止用コピー機天板がラス、冷凍用ショーケースなど様々な分野に利用されている。その中で、タッチパネルに関しては、IT化、モパイル化が進むにつれ、精報携帯端末(PDA)、電子手帳、携帯電話、デジタルカメラ、FA機器、カーナビゲーションなどへの搭載が急速に増えてきている。

## [0003]

タッチパネルの基本構成を図1に示す。図1においては、入力側のフィルム1上にフィルム用導電膜2を有する上部電極3とがラス基板5上に透明導電膜4を有する下部電極6と 50

がドットスペーサイを挟み込んで対向し、指や入力ペン8などで入力する際の圧力により上部電極8が んで、下部電極6と接することにより、その位置を電気的に検出するものである。

[0004]

近年、モバイル機器への用途に対しては、ますます小型・軽量・薄型化が要求されてあり、ガラス基板5の厚さも1、1 mmから、0、5~0、7 mm程度まで薄くなってきている。しかし、ガラス基板5の厚さを薄くしていくと、強度が低下し、使用中または携帯中の落下などにより割れるという不具合があった。

[0005]

上記問題を解決するために、ガラス基板の強度を高める方法として、ガラス基板表面に圧縮応力層を形成させる方法が一般的に知られている。前記ガラス基板表面に圧縮応力層を形成させる方法としては、軟化点付近まで加熱したガラス基板表面を風冷などにより急速に冷却する風冷強化法と、ガラス転移点以下の温度でイオン交換によりガラス基板表面にイオン半径のより大きいアルカリイオンを導入する化学強化法が代表的である。前述したように、ガラス基板の厚さが薄くなる場合、風冷強化法では、風冷過程において表面と内部の温度差がつきにくく目的の強度が得られにくい。そのため、後者の化学強化法による強化が通常行われている。

[00006]

一方、ガラス基板上に形成される透明導電膜には、ITO膜や酸化スズ膜が広く使われている。酸化スズ膜は、ITO膜と比べて、真空プロセスを使わない常圧CVD法で成膜できるため、量産性、コスト的に優れているとともに、性能的にも耐磨耗性や熱的・化学的耐久性に優れた特徴をもっている。

[0007]

しかし、常圧CVD法により酸化スズ膜を成膜する場合、生産性や膜性能を考慮すると成膜温度を高くする必要がある。その場合、一般的に使用されているソーダライムがラスをガラス基板として用いた場合、強度向上の目的であらかじめ化学強化されていたとしても、成膜工程で高温にさらされることによって表面の圧縮応力層が緩和され、せっかく向上させた強度が低下する問題があった。つまり、酸化スズ膜の生産性や膜性能とガラス基板の強度とを両立させることが困難であった。

[0008]

上記課題に対しては、酸化スズ膜を形成した後に化学強化する方法が開示されている(例えば、特許文献1、および特許文献2参照。)。この方法であれば、化学強化した後には高温の成膜プロセスを通らないため、ガラス基板の強度低下は起こりにくい。しかし、必然的に膜を介して化学強化するため、ガラス単体の場合と比べてイオン交換が困難になることが予想される。また、イオン交換が可能であったとしても、膜中にもアルカリイオンが含まれるため、膜の性能面での信頼性が劣ることが予想される。

[0009]

また、ソーダライムガラス以外のガラスをタッチパネルのガラス基板に適用した例が開示されている(例えば、特許文献 3 参照。)。しかし、強度向上目的ではないため化学強化処理は施されていない。

[0010]

【特許文献 1 】特開平 9 - 5 9 0 4 3 号公報

【特許文献2】特開平10-231147号公報

【特許文献3】特開平8-119674号公報

【発明が解決しようとする課題】

本発明は、前述の課題を解消しようとするものであり、常圧CVD法などの高温で成膜される工程においても、化学強化されたガラス基板の強度を損なうことなく、ガラス基板の厚さを薄くしたとしても、タッチパネルの実用強度を十分満足できる透明導電膜付き化学強化ガラス基板とその製造方法を提供することを目的とする。

[0011]

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## 【課題を解決するための手段】

本発明は、ガラス基板を化学強化することにより化学強化ガラス基板が形成され、前記化学強化ガラス基板上に透明導電膜が形成されてなる透明導電膜付き化学強化ガラス基板であって、前記透明導電膜付き化学強化ガラス基板は、質量%表示で2~7%のNa2Oおよび0~3%のLi2Oを含有し、歪点が550℃以上であり、かつ表面圧縮応力が200~800MPaである透明導電膜付き化学強化ガラス基板を提供する。

## [0012]

また、本発明は、ガラス基板を化学強化することにより化学強化ガラス基板を形成し、前記化学強化ガラス基板上に、常圧CVD法により透明導電膜を形成することを特徴とする透明導電膜付き化学強化ガラス基板の製造方法であって、前記透明導電膜付き化学強化ガラス基板は質量%表示で2~7%のNa2Oおよび0~3%のLi2Oを含有し、歪点が550℃以上であり、かつ表面圧縮応力が200~800MPaであることを特徴とする透明導電膜付き化学強化ガラス基板の製造方法を提供する。

#### [0013]

#### 【発明の実施の形態】

本発明の透明導電膜付き化学強化ガラス基板は、ガラス基板を化学強化する、例えば加熱された硝酸カリウム溶触塩にガラス基板を浸漬して、ガラス基板表層中のナトリウムイオンおよびリチウムイオンと溶触塩中のカリウムイオンとをイオン交換する、ことにより化学強化ガラス基板とした後、前記化学強化ガラス基板上に透明導電膜を成膜して得られる。好ましい成膜法は常圧CVD法である。

#### [0014]

前記ガラス基板の厚さは、 0 . 2~1 . 1 mmであることが好ましい。ガラス基板の厚さを上記範囲とすることにより、タッチパネル等の製品の軽量化に寄与きる。また、風冷強化では形成することができない厚さの圧縮応力層を化学強化により形成させることができる。 0 . 2 mm未満では、化学強化しても実用強度の観点から満足できなくなるおそれがある。また、前記ガラス基板の厚さが 0 . 2~0 . 7 mmといった薄板に、特に化学強化が有効である。

#### [0015]

なお、未強化ガラス基板の厚さは、それが化学強化された化学強化がラス基板の厚さと同じであり、さらにその上に透明導電膜が形成された透明導電膜付き化学強化ガラス基板の厚さとも同じである。同様にして、密度、歪点といった物性も三者間で同じである。また、未強化ガラス基板と化学強化ガラス基板とではでく薄い表層において微視的に化学組成が異なるが、ガラス基板全体としての化学組成は実質的に変化しない。また、化学強化ガラス基板と透明導電膜付きガラス基板とでは、ごく薄い透明導電膜の有無の点で微視的に化学組成が異なるが、ガラス基板と体としての化学組成は実質的に変化しない。すなわち、Na2O含有量、K2O含有量をはじめとするガラス基板の化学組成は、前記三者間で同じである。

## [0016]

透明導電膜付き化学強化がラス基板の表面圧縮応力は、200~800MPのであることが、タッチパネル等の実用強度の観点から必須であり、好ましくは300~600MPのである。また、透明導電膜形成後も表面圧縮応力を上記範囲とするためには、透明導電膜形成前の化学強化がラス基板やのものの表面圧縮応力は、200~800MPのであることが好ましく、さらに好ましくは300~600MPのである。化学強化がラス基板とは300~600MPのである。化学強化がラス基板に常圧CVD法で透明導電膜を形成する場合、成膜中にがラス基板が高温となるため、応用を指面が起こりやすくなり、化学強化処理で得られた強度を維持できなくなるあそれがある。よって、後述するように、かラス基板の歪点を550℃以上とすることにより、成膜後であっても、表面圧縮応力を上記範囲とすることが可能となる。

#### [0017]

透明導電膜付き化学強化がラス基板の圧縮応力層の深さは、15μm未満であると十分な化学強化の効果が得られないが、120μm超ではさらなる強度向上の効果が望めず、経

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済的でない。さらに、生産効率の観点から、大きいサイズの透明導電膜付き化学強化ガラス基板を後工程にて所望のサイズに切断することが行われているが、圧縮応力層の深さが120μmを越えると切断しにくくなる。強化性能と切断性とを考慮すると、透明導電膜付き化学強化ガラス基板の圧縮応力層の深さは、好ましくは30~100μm、さらに好ましくは30~70μmであり、特に好ましくは30~50μmである。圧縮応力層の深さは、高温での成膜によって実質的に変化しない。

[0018]

また、透明導電膜付き化学強化ガラス基板に用いられるガラス基板の歪点は、550℃以上である。550℃未満であると、常圧CVD法での成膜中にガラス基板が高温となる際に応力緩和が起こりやすくなり、化学強化工程で得られた強度が低下するおそれがある。なお、ガラス基板の歪点とは、成膜前かつ化学強化前における歪点を意味しており、化学強化後かつ成膜後であっても実質的にほとんど変化しない。

[0019]

本発明の透明導電膜付き化学強化ガラス基板が製品の軽量化に寄与するためには、ガラス基板の密度は低い方が好ましく、具体的には、2.4~2.69/cm³であることが好ましい。

[0020]

以下に本発明のガラス基板の化学組成について詳しく説明する。なお、以下における成分割合は、質量%表示である。

[0021]

No.2 Oは、イオン交換により表面圧縮応力層を形成させるための必須成分である。また、ガラスの溶触性を著しく向上させる成分でもある。2%より少ないと、イオン交換が困難となり所望の表面圧縮応力層が得られない。7%より多いと、歪点が低くなるだけでなく、ガラス基板の耐候性が低下する。

[0022]

 $Li_2$  Oは、必須成分ではないが、No. $_2$  Oと同じように、イオン交換により表面圧縮応力層を形成させるための成分である。また、ガラスの溶融性を著しく向上させる成分でもある。 8%より多いと、歪点が低下するおそれがある。

[0023]

K<sub>2</sub> Oは、溶触性を向上させる成分であるとともに、化学強化におけるイオン交換速度を向上させ、所望の表面圧縮応力と圧縮応力層の深さを得るために必要な成分である。4 %より少ないと、溶触性が惡化するとともにイオン交換速度が低下し好ましくない。1 3 %より多いと、歪点が低くなるおそれがある。

[0024]

 $SiO_2$ は、ガラスの骨格を構成する成分である。45%より少ないと、歪点が低くなるとともに、耐候性が惡化する傾向がある。70%より多いと、ガラスの粘性が増大し溶融性が着しく惡化する。

[0025]

 $A \mid_2 O_3$  は、歪点を高くする成分であるとともに、イオン交換速度を向上させる成分である。 2 % より少ないと歪点が低くなり、イオン交換速度向上の効果も得られなくなり好 4 ましくない。  $2 \mid_2 0$  %より多いと、ガラスの粘性が高くなるため、均質な溶融が困難になる

[0026]

 $B_2$   $O_3$  は、必須成分ではないが、添加することにより溶融性が向上するので 6 %まで含有させることができる。 6 %より多いと、溶融時の揮散が激しくなるとともに、歪点が低下するおそれがあるので好ましくない。

[0027]

区 r O 2 は、 必須成分ではないが、 歪点を高める成分であるとともにイオン交換速度を向上させる成分である。 6 %より多いと、さらなるイオン交換速度向上の効果は得られないとともに、 密度が増大し、溶触性も惡化し、 未溶触物としてがラス中に残るので好ましく

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なり。

M90+Ca0+SFO+BaO、すなわちM90とCaOとSFOとBaOとの合計の含有量は10~25%であることが好ましい。M90、CaO、SFOおよびBaOは、溶触性を向上させる成分であるとともに、歪点の調節に有効な成分である。これらの合量が10%より少ないと溶触性が惡化するので好ましくない。これらの合量が25%より多いと、失透しやすくなるうえ、歪点が低下するおそれがある。さらにイオン交換速度が低下するおそれもある。また密度を下げるためにはSFOは3%以下、BaOは2%以下であることが好ましい。

#### [0028]

上記成分以外の任意の成分として、本発明の目的を損なわなり範囲で、ガラスの溶融の際の清澄削として、 $SO_3$ 、 $Sb_2O_3$ 、 $AS_2O_3$ 、塩化物、フッ化物などを適宜含有してもより。ただし、タッチパネルの視認性を上げるため、可視域に吸収をもつドミ $_2O_3$ 、NiO、 $Cr_2O_3$  などの原料中の不純物として退入するような成分はできるだけ減らすことが好ましく、各々O. 15%以下、特にO. 05%以下であることが好ましい。

#### [0029]

先に触れたとあり、Noline O およびLi $_2$  O は、化学強化を行うことにより、 $K_2$  O へとイオン交換される。イオン交換後の化学強化がラス基板の表面のごく薄り領域では、 $K_2$  O の成分が多くなっているが、化学強化がラス基板全体の組成としては実質的に変化することはない。

### [0030]

本発明に用いられる化学強化前(すなわち未処理)のガラス基板の製造方法は特に限定されないが、例えば、種々の原料を適量調合し、約1500~1600℃に加熱し溶融した後、脱泡、 などにより均質化し、周知のフロート法、ダウンドロー法、プレス法などによって板状に成形する。徐冷後、必要に応じて所望のサイズに切断、研磨加工を施し、ガラス基板が得られる。

## [0031]

さらに所定の化学強化の方法により、ガラス基板に化学強化を施す。前記化学強化の方法としては、ガラス基板表層内のNa2 OおよびLi2 OとK2 Oとをイオン交換することができれば特に限定されないが、具体的には、加熱された硝酸カリウム溶触塩にガラス基板を浸漬することにより、ガラス中のNa2 OおよびLi2 Oと溶触塩中のK2 Oとをイオン交換する方法が挙げられる。ガラス基板に所望の表面圧縮応力を有する化学強化層を設けるためには、ガラス基板の厚さによっても変動するが、400~550℃の硝酸カリウム溶液に2~10時間ガラス基板を浸漬させることが好ましい。

#### [0032]

ガラス基板を化学強化することにより化学強化ガラス基板を形成した後、前記化学強化ガラス基板上に透明導電膜を形成する。透明導電膜を形成する方法としては、常圧CVD法を対って基板上に常圧CVD法を用いて形成する場合は、以下のような方法が用いられる。まず、化学強化ガラス基板を、ペルト式加熱炉に投入し、キャリアガスとともに原料がる。なインジェクタから噴霧することにより化学強化ガラス基板上に酸化スズ膜を成膜する。原料ガスとして用いられる酸化スズ原料は特に限定されず、四塩化スズなどのスズ原料は特に限定されず、四塩化スズなどのスズルン・カール化スズなどを用いることができる。また、膜抵抗の調整のため、フッ素、アルキル化スズなどを用いることができる。前記常圧CVD法にあける化学強化ガラス基板の温度は500~550℃であることが好ましい。

## [0033]

透明導電膜としては、耐磨耗性や熱的・化学的耐久性に優れた酸化スズ膜が好ましく用いられる。前記透明導電膜の厚さは、タッチパネルとして用いる場合、10~20mmであることが透過率の点で好ましい。

## [0034]

さらに、ガラス基板から酸化スズ膜などの透明導電膜へのアルカリマイグレーションを防 50

止するため、酸化ケイ素などのアルカリパリア層をガラス基板と透明導電膜との間に設けてもよい。この場合、例えば、別のインジェクタから、モノシランと酸素とからなるガスを噴霧することで同時に成膜することができる。前記酸化ケイ素のアルカリパリア層の膜厚は、タッチパネルとして用いる場合、40~60mmであることが光学特性の点で好ましい。

[0035]

本発明の透明導電膜付き化学強化がラス基板は、タッチパネル、ディスプレイ、太陽電池 用カパーがラス、帯電防止用コピー機天板がラス、冷凍用ショーケースなどの種々の用途 に使用することができる。

[0036]

また、本発明の透明導電膜付き化学強化がラス基板のシート抵抗値は、タッチパネルとして用いる場合、300~2000Ω/□であることが好ましい。また、本発明の透明導電膜付き化学強化がラス基板の可視光線での最高透過率(裏面コートのない条件において、400~700nmの範囲における透過率のうち、最も高い透過率を意味する。)は、タッチパネルとして用いる場合、87~95%であることが視認性の点で好ましい。

[0037]

【実施例】

以下に実施例(例1~6)および比較例(例7~10)を学げて、本発明を詳細に説明する。 ただし、本発明はこれに限定されない。

[0038]

表1の組成(単位:質量%)になるように、酸化物、水酸化物、炭酸塩、硝酸塩等一般に使用されているガラス原料を通宜選択し、ガラスとして2k分となるように秤量および混合した。ついで、白金製るつぼに入れ、1600℃の抵抗加熱式電気炉に投入し、5時間溶融し、脱泡、均質化した後、型材に流し込み、所定の温度で徐冷し、ガラスプロックを得た。このガラスプロックからサイズが55×55mm×厚み0、7mmになるように切断、研削し、最後に両面を鏡面に加工し、ガラス基板を得た。このとき、例1~10の可視光線での最高透過率は、91~92%であった。可視光線での最高透過率は、分光光度計UV1600(割津製作所製)を用いて測定した。

[0039]

【表1】

衩   】								,		
	例 1	例 2	例3	例 4	例5	例 6	例 7	例8	例9	例 10
$SiO_2$	61.0	62.0	57.0	65.0	63.0	68.0	72.5	65.5	64.0	56.0
Al <sub>2</sub> O <sub>3</sub>	9.5	7.5	12.5	4.0	11.0	3.0	1.5	17.0	16.5	11.0
B <sub>2</sub> O <sub>3</sub>	0	1.0	0.5	0	0_	0	0	0	0	6.0
Li <sub>2</sub> O	0	00	0.5	1.0	0	0_	0_	5.0	0	0
Na <sub>2</sub> O	5.0	6.0	4.0	3.0	7.0	5.5	13.5	8.5	11.5	0.5
K <sub>2</sub> O	9.5	8.0	8.0	12.0	5.0	7.5	0.5	0	3.0	0
MgO	5.0	8.0	4.5	5.5	5.0	7.0	4.0	3.0	4.0	2.0
CaO	6.0	1.0	7.0	5.0	5.0	4.5	8.0	0	1.0	3.0
SrO	1.5	3.0	2.0	1.0	2.0	0.5	0	0	0_	6.5
ВаО	0.5	1.0	2.5	0	1.0	2.0	0	0	0	15.0
その他	2.0	2.5	1.5	3.5	1.0	2.0	0	1.0	0	0

[0040]

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前記がラス基板の密度および歪点を測定した。密度は約20分の塊をアルキメデス法によって測定した。歪点は繊維引き伸ばし法(JIS R3103-2)によって測定した。その結果を表2に示す。

[0041]

ついで、前記ガラス基板を、例1~6および例9、10については、500℃に加熱保持した硝酸カリウム溶配塩中に5時間浸漬して化学強化処理を施し、化学強化ガラス基板を得た。例7、8については、450℃に加熱保持した硝酸カリウム溶配塩中に5時間浸漬して化学強化処理を施し、化学強化ガラス基板を得た。次にベルト炉に化学強化ガラス基板を投入し、530℃に加熱した成膜ゾーンで、常圧CVD法によって、四塩化スズ、水、メタノールとフッ化水素を噴霧し、化学ガラス強化基板上に酸化スズ膜を成膜し、酸化スズ膜付き化学強化ガラス基板を得た。

[0042]

例1~10 において、得られた酸化スズ膜付き化学強化ガラス基板について、シート抵抗値および可視光線での最高透過率を測定した。シート抵抗値は、ロレスタMCP-T250(三菱化学社製)により四探針法を用いて測定した。また、可視光線での最高透過率は、分光光度計UV1600(18津製作所製)を用いて、裏面コートがない条件において測定した。

[0043]

その結果、例 1 ~ 1 0 における酸化スズ膜付き化学強化ガラス基板の可視光線での最高透過率は、例 1 ~ 1 0 において 9 0 %以上であり、シート抵抗値は 8 0 0 ~ 1 2 0 0  $\Omega$  /  $\Box$  であり、タッチパネルの下部電極として充分な性能が得られていることを確認した。

[0044]

ついで、例1~10における酸化スズ膜付き化学強化ガラス基板について、表面圧縮応力 あよび圧縮応力層の深さを測定し、あらかしめ成膜前に測定した表面圧縮応力と成膜後の 表面圧縮応力との比(成膜後の表面圧縮応力/成膜前の表面圧縮応力。以下、圧縮応力比 という。)を求めた。表面圧縮応力および圧縮応力層の深さの測定は、切り出した薄片の 一部を用いて表面応力計FSM-60-V(折原製作所製)にて行った。その結果を表 2 に示す。

[0045]

さらに、得られた例1~10の酸化スズ膜付き化学強化ガラス基板の破壊応力を同心円曲け試験法にて測定した。すなわち、直径46mmの支持リング上に酸化スズ膜付き化学強化ガラス基板を配置し、直径19mmのリングを用いて膜面側に1mm/minのクロスヘッドスピードにて負荷をかけ破壊したときの破壊応力を求めた。なお、破壊応力は各10枚ずつ酸化スズ膜付き化学強化ガラス基板を試験し平均値を求めた。破壊応力は、実用上、350MPの以上であることが好ましい。その結果を表2に示す。

[0046]

【表2】

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		7		1	T	T .		1	1	
	例1	例2	例3	例4	例 5	例6	例 7	例8	例 9	例 10
歪点	590	570	580	550	590	570	510	480	570	630
(°C)										
密度	2.55	2.54	2.60	2.55	2.54	2.52	2.50	2.45	2.46	2.77
(g/cm³)				ļ						
表面圧縮応力	390	430	390	340	530	450	150	170	190	
(MPa)										
圧縮応力層の	40	80	60	100	30	50	20	130	20	-
深さ(μm)								<u> </u>		
圧縮応力比	0.98	0.96	0.95	0.94	0.99	0.98	0.71	0.55	0.96	-
破壊応力	470	520	490	500	430	480	290	320	180	160
(MPa)									<u></u>	

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#### [0047]

表2に示すように、例1~6は、ガラス基板の歪点が550℃以上であるため、圧縮応力比がほぼ1に近く成膜プロセスを通しても表面圧縮応力の低下は起こっておらず、応力が緩和されていなかった。その結果、破壊応力も高くなり、実用上十分な強度であることが示された。さらに圧縮応力層の深さが好適な範囲となっているため、例1~6の透明等電膜付き化学強化がラス基板をホイールカッタにて切断したところ、化学強化前のガラス基板のみで通常切断できているホイール圧に対して1.2~1.5倍のホイール圧にて問題なく切断できた。

## [0048]

これに対し、ガラス基板がソーダライムガラスである例では、歪点が510℃であるため、圧縮応力比が低く、成膜プロセスを通すと表面圧縮応力の低下が起こり、成膜中に応力が緩和されていることが示された。その結果、破壊応力も低かった。例8は、圧縮応力に放け、ガラス基板の歪点が480℃であるために、例7と同様に応力を分が、がある。また、透明導電膜付きを対応である。また、透明導電膜付きを対応になり、破壊応力も低かった。また、透明等電膜付りにないが、が、透明できなかった。例9は、からに切りにはがある。例9は、が、できなかった。例9は、が、できなが、できなかった。例9は、Na20含有量が小さいため、化学強化処理しても圧縮応力層が判別できるほど形成されていなく、破壊応力もかなり低かった。

[0049]

### 【発明の効果】

本発明の透明導電膜付き化学強化がラス基板は、ガラス基板の歪点が550℃以上のため、成膜中に応力緩和が起こりにくく、化学強化処理で得られた表面圧縮応力を維持できるので、ガラス基板の厚さを薄くしても実用上十分な強度を有する。よって、本発明の透明等電膜付き化学強化ガラス基板は、タッチパネル用部材として好適である。また、従来より高温で成膜できる可能性が広がることにより、生産性向上が期待できる。また、透明等電膜以外の膜、例えば、アルカリバリア膜、反射防止膜、絶縁膜等の成膜温度範囲も広がる。さらに化学強化も同様に高温処理が可能となる。

【図面の簡単な説明】

【図1】タッチパネルの構成を説明する図

【符号の説明】

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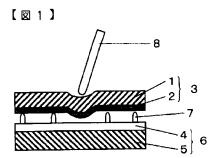
1:フィルム

2:フィルム用導電膜

3 : 上部電極 4 : 透明導電膜 5: ガラス基板 6:下部電極

7:ドットスペーサ

8:入カペン



テーマコード(参考)

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(71)Applicant: ASAHI GLASS CO LTD

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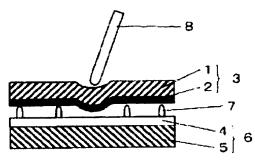
> **AIZAWA HARUO** MAEDA TAKASHI

# (54) CHEMICALLY STRENGTHENED GLASS SUBSTRATE WITH TRANSPARENT CONDUCTIVE FILM AND ITS MANUFACTURING PROCESS

(57) Abstract:

PROBLEM TO BE SOLVED: To retain surface compressive stress without causing decrease in strength under a film-forming condition for a

transparent conductive film.



SOLUTION: A chemically strengthened glass substrate with a transparent conductive film is manufactured by forming the chemically strengthened glass substrate by chemically strengthening a glass substrate and forming the transparent conductive film on the chemically strengthened glass substrate. The chemically strengthened glass substrate contains 2-7 mass% Na2O and 0-3 mass% Li2O and has a strain point of ≥50°C and a surface compressive strength of 200-800 MPa.

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## **CLAIMS**

# [Claim(s)]

[Claim 1]

It is a chemically-strengthened-glass board with a transparent conducting film with which a chemically-strengthened-glass board is formed and it comes to form a transparent conducting film on said chemically-strengthened-glass board by carrying out chemical strengthening of the glass substrate,

A chemically-strengthened-glass board with a transparent conducting film whose strain point said chemically-strengthened-glass board with a transparent conducting film contains 2 to 7% of  $Na_2O$ , and 0 to 3% of  $Li_2O$  by mass % display, and is not less than 550 \*\* and whose surface pressure shrinkage stress is 200 - 800MPa.

[Claim 2]

The 0.2-1.1-mm-thick chemically-strengthened-glass board [ said chemically-strengthened-glass board with a transparent conducting film ] with a transparent conducting film according to claim 1.

[Claim 3]

The chemically-strengthened-glass board with a transparent conducting film according to claim 1 or 2 with which said chemically-strengthened-glass board with a transparent conducting film contains 4 to 13% of  $K_2O$  by mass % display.

[Claim 4]

Said chemically-strengthened-glass board with a transparent conducting film by mass % display 45 to 70% of SiO<sub>2</sub>, The chemically-strengthened-glass board with a transparent conducting film according to claim 3 which contains further 2 to 20% of aluminum<sub>2</sub>O<sub>3</sub>, 0 to 6% of B<sub>2</sub>O<sub>3</sub>, 0 to 6% of ZrO<sub>2</sub>, and 10 to 25% of MgO+CaO+SrO+BaO. [Claim 5]

A chemically-strengthened-glass board with a transparent conducting film given in any 1 clause of Claims 1-4 whose density of said chemically-strengthened-glass board with a transparent conducting film is 2.4 - 2.6 g/cm<sup>3</sup>.

[Claim 6]

A chemically-strengthened-glass board with a transparent conducting film given in any 1 clause of Claims 1-5 whose depth of a compressive stress layer of said chemically-strengthened-glass board with a transparent conducting film is 15-120 micrometers. [Claim 7]

A chemically-strengthened-glass board with a transparent conducting film given in any 1 clause of Claims 1-6 in which said transparent conducting film is a tin-oxide film. [Claim 8]

It is a manufacturing method of a chemically-strengthened-glass board with a transparent conducting film which forms a chemically-strengthened-glass board and forms a transparent conducting film with an ordinary pressure CVD method on said chemically-strengthened-

glass board by carrying out chemical strengthening of the glass substrate,

A manufacturing method of a chemically-strengthened-glass board with a transparent conducting film characterized by the following.

Said chemically-strengthened-glass board with a transparent conducting film is a mass % display, and are 2 to 7% of Na<sub>2</sub>O, and 0 to 3% of Li<sub>2</sub>O.

A strain point is not less than 550 \*\*, and surface pressure shrinkage stress is 200 - 800MPa.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Field of the Invention]

Especially this invention relates to a chemically-strengthened-glass board with a transparent conducting film suitable for touch panels, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]

the glass substrate with a transparent conducting film in which transparent conducting films, such as tin oxide and indium tin oxide (ITO), were formed on the glass substrate -- a touch panel, a display, the cover glass for solar cells, and antistatic -- business -- it is used for various fields, such as copy machine top-plate glass and a showcase for refrigeration. Loading to an information personal digital assistant (PDA), an electronic notebook, a cellular phone, a digital camera, FA apparatus, car navigation, etc. is increasing quickly as IT-izing and mobile-ization progress about a touch panel in it.

[0003]

The basic constitution of a touch panel is shown in <u>drawing 1</u>. In <u>drawing 1</u>, the upper electrode 3 which has the conducting film 2 for films on the film 1 of an input side, and the lower electrode 6 which has the transparent conducting film 4 on the glass substrate 5 put the dot spacer 7, and counters, The upper electrode 3 bends with the pressure at the time of inputting with a finger, the input pen 8, etc., and the position is electrically detected by touching the lower electrode 6.

[0004]

In recent years, to the use to mobile computing devices, small size, a light weight, and slimming down are demanded increasingly, and the thickness of the glass substrate 5 is also becoming thin from 1.1 mm to about 0.5-0.7 mm. However, when thickness of the glass substrate 5 was made thin, intensity fell and there was fault of being divided by fall under use or carrying, etc.

[0005]

In order to solve the above-mentioned problem, the method of making a compressive stress layer form in the glass substrate surface is generally known as a method of raising the intensity of a glass substrate. As a method of making a compressive stress layer forming in

said glass substrate surface, The thermal-tempering-by-air-jets method which cools quickly the glass substrate surface heated to near softening temperature by air blast quenching etc., and the chemical-strengthening method which introduces the larger alkaline ion of an ion radius into the glass substrate surface by ionic exchange at the temperature below a glass transition point are typical. As mentioned above, when the thickness of a glass substrate becomes thin, in a thermal-tempering-by-air-jets method, the target intensity is hard to be obtained that it is hard to attach the temperature gradient of the surface and an inside in an air-blast-quenching process. Therefore, strengthening by the latter chemical-strengthening method is usually performed.

[0006]

On the other hand, the ITO film and the tin-oxide film are widely used for the transparent conducting film formed on a glass substrate. Since a tin-oxide film can be formed with the ordinary pressure CVD method not using a vacuum process compared with an ITO film, it has mass production nature and the feature which was efficiently excellent in abrasion resistance, or thermal and chemical durability while excelling in cost.

However, when forming a tin-oxide film with an ordinary pressure CVD method, if productivity and film performance are taken into consideration, it is necessary to make forming temperature high. In that case, though chemical strengthening was beforehand carried out for the purpose of improving strength when the soda lime glass generally used was used as a glass substrate, by being exposed to an elevated temperature by stage film formation, the surface compressive stress layer was eased and there was a problem to which the intensity raised with much trouble falls. That is, it was difficult to reconcile the productivity of a tin-oxide film, and film performance and the intensity of a glass substrate. [0008]

To the aforementioned problem, after forming a tin-oxide film, the method of carrying out chemical strengthening is indicated (for example, refer to the patent documents 1 and patent documents 2.). Since it does not pass along a hot membrane formation process after carrying out chemical strengthening if it is this method, the strength reduction of a glass substrate does not happen easily. However, in order to carry out chemical strengthening via a film inevitably, it is expected that ionic exchange becomes difficult compared with the case of a glass simple substance. Since alkaline ion is contained also in a film even if ionic exchange is possible, it is expected that the reliability in respect of membranous performance is inferior.

The example which applied glass other than soda lime glass to the glass substrate of the touch panel is indicated (for example, refer to patent documents 3.). However, since it is not the improving strength purpose, chemical strengthening treatment is not performed.

[0010]

[Patent documents 1] JP,H9-59043,A

[Patent documents 2] JP,H10-231147,A

[Patent documents 3] JP,H8-119674,A

[Problem to be solved by the invention]

This invention tends to cancel above-mentioned SUBJECT.

Also in the process formed at elevated temperatures, such as an ordinary pressure CVD method, even if the purpose makes thickness of a glass substrate thin, without spoiling the intensity of the glass substrate by which chemical strengthening was carried out, it is providing the chemically-strengthened-glass board with a transparent conducting film with which it can be satisfied of the practical strength of a touch panel enough, and its manufacturing method.

[0011]

[Means for solving problem]

When this invention carries out chemical strengthening of the glass substrate, a chemically-strengthened-glass board is formed, Are a chemically-strengthened-glass board with a transparent conducting film with which it comes to form a transparent conducting film on said chemically-strengthened-glass board, and said chemically-strengthened-glass board with a transparent conducting film, 2 to 7% of Na<sub>2</sub>O and 0 to 3% of Li<sub>2</sub>O are contained by mass % display, a strain point is not less than 550 \*\*, and surface pressure shrinkage stress provides the chemically-strengthened-glass board with a transparent conducting film which is 200 -800MPa.

[0012]

This invention forms a chemically-strengthened-glass board by carrying out chemical strengthening of the glass substrate, It is a manufacturing method of the chemically-strengthened-glass board with a transparent conducting film forming a transparent conducting film with an ordinary pressure CVD method on said chemically-strengthened-glass board, Said chemically-strengthened-glass board with a transparent conducting film contains 2 to 7% of Na<sub>2</sub>O, and 0 to 3% of Li<sub>2</sub>O by mass % display, The manufacturing method of a chemically-strengthened-glass board with a transparent conducting film, wherein a strain point is not less than 550 \*\* and surface pressure shrinkage stress is 200 - 800MPa is provided.

[Mode for carrying out the invention]

The chemically-strengthened-glass board with a transparent conducting film of this invention, Carry out chemical strengthening of the glass substrate, for example, a glass substrate is immersed in the heated potassium nitrate fused salt, After [ which carries out ionic exchange of the sodium ion in a glass substrate surface and a lithium ion and the potassium ion in fused salt ] considering it as a chemically-strengthened-glass board especially more, it is obtained by forming a transparent conducting film on said chemically-strengthened-glass board. The desirable forming-membranes method is an ordinary pressure CVD method. [0014]

As for the thickness of said glass substrate, it is preferred that it is 0.2-1.1 mm. By making thickness of a glass substrate into a mentioned range, it is contribution \*\*\*\* to the weight saving of products, such as a touch panel. The compressive stress layer of the thickness which cannot be formed in thermal tempering by air jets can be made to form by chemical strengthening. There is a possibility that it may become impossible to be satisfied with less than 0.2 mm from a viewpoint of practical strength even if it carries out chemical strengthening. Especially chemical strengthening is effective in the sheet metal of 0.2-0.7 mm in the thickness of said glass substrate.

[0015]

It of the thickness of a non-tempered glass board is the same as that of the thickness of the chemically-strengthened-glass board by which chemical strengthening was carried out, and it is the same also as the thickness of the chemically-strengthened-glass board with a transparent conducting film with which the transparent conducting film was further formed on it. Similarly, physical properties, such as density and a strain point, are also the same among 3 persons. Although chemical composition differs microscopically in a very thin surface with a non-tempered glass board and a chemically-strengthened-glass board, the chemical composition as the whole glass substrate does not change substantially. Although chemical conducting film with a chemically-strengthened-glass board and a glass substrate with a transparent conducting film, the chemical composition as the whole glass substrate does not change substantially. That is, the chemical composition of glass substrates including Na<sub>2</sub>O

content and  $K_2O$  content is the same among said 3 persons. [0016]

As for the surface pressure shrinkage stress of a chemically-strengthened-glass board with a transparent conducting film, it is indispensable from a viewpoint of the practical strength of a touch panel etc. that it is 200 - 800MPa, and it is 300 - 600MPa preferably. In order for after transparent conducting film formation to make surface pressure shrinkage stress a mentioned range, it is desirable still more preferred that it is 200 - 800MPa, and the surface pressure shrinkage stress of the chemically-strengthened-glass board before transparent conducting film formation itself is 300 - 600MPa. Since a glass substrate serves as an elevated temperature during membrane formation when forming a transparent conducting film with an ordinary pressure CVD method on a chemically-strengthened-glass board, stress relaxation happens easily and there is a possibility that it may become impossible to maintain the intensity obtained by chemical strengthening treatment. Therefore, as mentioned later, even if it is after membrane formation by the strain point of a glass substrate being not less than 550 \*\*\*, it becomes possible to make surface pressure shrinkage stress into a mentioned range.

Although the effect of sufficient chemical strengthening is not acquired with it being less than 15 micrometers, the depth of the compressive stress layer of a chemically-strengthened-glass board with a transparent conducting film cannot expect an effect of the further improving strength at more than 120 micrometers, and is not economical. Although cutting the chemically-strengthened-glass board with a transparent conducting film of large size from a viewpoint of productive efficiency in the size of a request in a post process is performed, it will become difficult to cut if the depth of a compressive stress layer exceeds 120 micrometers. When strengthening performance and a sectility are taken into consideration, preferably, 30-100 micrometers, the depth of the compressive stress layer of a chemically-strengthened-glass board with a transparent conducting film is 30-70 micrometers still more preferably, and is 30-50 micrometers especially preferably. The depth of a compressive stress layer does not change with the membrane formation in an elevated temperature substantially. [0018]

The strain point of the glass substrate used for a chemically-strengthened-glass board with a transparent conducting film is not less than 550 \*\*. When a glass substrate becomes being less than 550 \*\* with an elevated temperature during membrane formation with an ordinary pressure CVD method, stress relaxation happens easily, and there is a possibility that the intensity obtained by the chemical strengthening process may fall. The strain point of a glass substrate means the strain point before membrane formation and chemical strengthening, and even if it is after chemical strengthening and membrane formation, it hardly changes substantially.

[0019]

In order for the chemically-strengthened-glass board with a transparent conducting film of this invention to contribute to the weight saving of a product, the lower one of the density of a glass substrate is preferred, and, specifically, it is preferred that it is 2.4 - 2.6 g/cm<sup>3</sup>. [0020]

The chemical composition of the glass substrate of this invention is explained in detail below. The following ingredient rates are mass % displays.

[0021]

 $Na_2O$  is an essential ingredient for making a surface pressure shrinkage stress layer form by ionic exchange. It is also an ingredient which raises the melting nature of glass remarkably. If less than 2%, ionic exchange will become difficult and a desired surface pressure shrinkage stress layer will not be obtained. If more than 7%, a strain point not only becomes low, but the weatherability of a glass substrate will fall.

## [0022]

Although Li<sub>2</sub>O is not an essential ingredient, it is an ingredient for making a surface pressure shrinkage stress layer form by ionic exchange like Na<sub>2</sub>O. It is also an ingredient which raises the melting nature of glass remarkably. When more than 3%, there is a possibility that a strain point may fall.

[0023]

K<sub>2</sub>O is an ingredient required in order to raise the ion-exchange rate in chemical strengthening and to obtain desired surface pressure shrinkage stress and the depth of a compressive stress layer while being an ingredient which raises melting nature. If less than 4%, while melting nature gets worse, an ion-exchange rate falls and it is not desirable. When more than 13%, there is a possibility that a strain point may become low. [0024]

SiO<sub>2</sub> is an ingredient which constitutes the skeleton of glass. If less than 45%, while a strain point will become low, there is a tendency for weatherability to get worse. If more than 70%, the viscosity of glass will increase and melting nature will get worse remarkably. [0025]

aluminum<sub>2</sub>O<sub>3</sub> is an ingredient which raises an ion-exchange rate while being an ingredient which makes a strain point high. If less than 2%, it becomes low, the effect of the improvement in an ion-exchange rate is also no longer acquired, and a strain point is not preferred. Since the viscosity of glass will become high if more than 20%, homogeneous melting becomes difficult.

[0026]

Since melting nature improves by adding,  $B_2O_3$  can be made to contain to 6%, although it is not an essential ingredient. If more than 6%, while the vaporization at the time of melting will become intense, since there is a possibility that a strain point may fall, it is not desirable. [0027]

Although ZrO<sub>2</sub> is not an essential ingredient, it is an ingredient which raises an ion-exchange rate while being an ingredient which raises a strain point. If more than 6%, since density increases, melting nature also gets worse and the effect of the further improvement in an ion-exchange rate remains into glass as non-melt, it is not preferred while not being obtained. As for the content of the sum total of MgO+CaO+SrO+BaO, i.e., MgO, CaO, and SrO and BaO, it is preferred that it is 10 to 25%. MgO, CaO, SrO, and BaO are an ingredient effective in regulation of a strain point while being ingredients which raise melting nature. Since melting nature will get worse if there are few these total amounts than 10%, it is not desirable. If there are more these total amounts than 25%, it will become easy to devitrify, and also there is a possibility that a strain point may fall. There is also a possibility that an ion-exchange rate may furthermore fall. In order to lower density, it is preferred that SrO is 3% or less and BaO is 2% or less.

[0028]

As arbitrary ingredients other than the above-mentioned ingredient, SO<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>, a chloride, fluoride, etc. may be suitably contained as a clarifying agent in the case of melting of glass in the range which does not spoil the purpose of this invention. However, Fe<sub>2</sub>O<sub>3</sub> which has absorption in a visible range in order to raise the visibility of a touch panel, As for an ingredient which is mixed as an impurity in raw materials, such as NiO and Cr<sub>2</sub>O<sub>3</sub>, reducing as much as possible is preferred, and it is respectively preferred that it is especially 0.05% or less 0.15% or less.

[0029]

Ionic exchange of  $Na_2O$  and the  $Li_2O$  is carried out by performing chemical strengthening to  $K_2O$  as touched previously. In the very thin field of the surface of the chemically-strengthened-glass board after ionic exchange, although the ingredient of  $K_2O$  has increased,

as a presentation of the whole chemically-strengthened-glass board, it does not change substantially.

[0030]

Although the manufacturing method in particular of the glass substrate before chemical strengthening used for this invention (that is, unsettled) is not limited, For example, a proper quantity of various raw materials are prepared, and after heating and carrying out melting to about 1500-1600 \*\*, it uniforms by degassing, stirring, etc. and fabricates to tabular by the well-known float glass process, the down draw method, the pressing method, etc. Cutting and polishing work are performed to desired size after annealing if needed, and a glass substrate is obtained.

[0031]

By the method of further predetermined chemical strengthening, chemical strengthening is performed to a glass substrate. As the method of said chemical strengthening, especially if ionic exchange of Na<sub>2</sub>O and Li<sub>2</sub>O, and K<sub>2</sub>O in a glass substrate surface can be carried out, will not be limited, but. The method of carrying out ionic exchange of Na<sub>2</sub>O in glass and Li<sub>2</sub>O, and the K<sub>2</sub>O in fused salt is mentioned by specifically immersing a glass substrate in the heated potassium nitrate fused salt. In order to provide the chemical-strengthening layer which has desired surface pressure shrinkage stress in a glass substrate, it changes also with the thickness of a glass substrate, but it is preferred to make a 400-550 \*\* potassium nitrate solution immerse a glass substrate for 2 to 10 hours.

After forming a chemically-strengthened-glass board by carrying out chemical strengthening of the glass substrate, a transparent conducting film is formed on said chemically-strengthened-glass board. As a method of forming a transparent conducting film, an ordinary pressure CVD method is used preferably. The following methods are used, when using an ordinary pressure CVD method and forming a tin-oxide film on a chemically-strengthened-glass board, using the tin oxide as a material of a transparent conducting film. First, a chemically-strengthened-glass board is thrown into a belt type heating furnace, and a tin-oxide film is formed on a chemically-strengthened-glass board by spraying material gas from an injector with carrier gas. As material gas, the tin-oxide raw material in particular used is not limited, but can use tin salt ghosts, such as a tin tetrachloride, alkylation tin, etc. Minor constituents, such as fluoride and antimony, can be added for adjustment of membrane resistance. As for the temperature of the chemically-strengthened-glass board in said ordinary pressure CVD method, it is preferred that it is 500-550 \*\*.

As a transparent conducting film, the tin-oxide film excellent in abrasion resistance, or thermal and chemical durability is used preferably. As for the thickness of said transparent conducting film, when using as a touch panel, it is preferred that it is 10-20 nm in respect of transmissivity.

[0034]

In order to prevent the alkali migration from a glass substrate to transparent conducting films, such as a tin-oxide film, alkali barrier layers, such as a silicon oxide, may be provided between a glass substrate and a transparent conducting film. In this case, membranes can be simultaneously formed by, for example, spraying the gas which consists of a mono silane and oxygen from another injector. As for the thickness of the alkali barrier layer of said silicon oxide, when using as a touch panel, it is preferred that it is 40-60 nm in respect of an optical property.

[0035]

the chemically-strengthened-glass board with a transparent conducting film of this invention - a touch panel, a display, the cover glass for solar cells, and antistatic -- business -- it can be

used for various uses, such as copy machine top-plate glass and a showcase for refrigeration. [0036]

As for the sheet resistance values of the chemically-strengthened-glass board with a transparent conducting film of this invention, when using as a touch panel, it is preferred that they are 300-2000ohm/\*\*. The highest transmissivity in the visible light of the chemically-strengthened-glass board with a transparent conducting film of this invention (on conditions without a rear-face coat) The highest transmissivity is meant among the transmissivity in the range of 400-700 nm. When using as a touch panel, it is preferred that it is 87 to 95% in respect of visibility.

[0037]

[Working example]

An embodiment (Examples 1-6) and a comparative example (Examples 7-10) are given to below, and this invention is explained in detail. However, this invention is not limited to this. [0038]

raw materials for glass currently generally used, such as an oxide, hydroxide, carbonate, and a nitrate, are chosen suitably, and it is set to 2 kg as glass so that it may become the presentation (unit: mass %) of Table 1 -- as -- weighing -- and it mixed. Subsequently, it put into the crucible made from platinum, it supplied to a 1600 \*\* resistance heating type electric furnace, and melting was carried out to it for 5 hours, degassing and after uniforming, it slushed into the mold material, and cooled slowly at a predetermined temperature, and the glass block was obtained. It cut and ground so that size might be set to 55x55 mmx0.7 mm in thickness from this glass block, and finally both sides were processed on the mirror plane, and the glass substrate was obtained. At this time, the highest transmissivity in the visible light of Examples 1-10 was 91 to 92%. The highest transmissivity in visible light was measured using spectrophotometer UV1600 (made by Shimadzu).

[Table 1]

	例 1	例 2	例3	例 4	例 5	例 6	例 7	例8	例 9	例 10
SiO <sub>2</sub>	61.0	62.0	57.0	65.0	63.0	68.0	72.5	65.5	64.0	56.0
Al <sub>2</sub> O <sub>3</sub>	9.5	7.5	12.5	4.0	11.0	3.0	1.5	17.0	16.5	11.0
B <sub>2</sub> O <sub>3</sub>	0	1.0	0.5	0	0	0	0	0	0	6.0
Li <sub>2</sub> O	0	0	0.5	1.0	0	0	0	5.0	0	0
Na <sub>2</sub> O	5.0	6.0	4.0	3.0	7.0	5.5	13.5	8.5	11.5	0.5
K <sub>2</sub> O	9.5	8.0	8.0	12.0	5.0	7.5	0.5	0	3.0	0
MgO	5.0	8.0	4.5	5.5	5.0	7.0	4.0	3.0	4.0	2.0
CaO	6.0	1.0	7.0	5.0	5.0	4.5	8.0	0	1.0	3.0
SrO	1.5	3.0	2.0	1.0	2.0	0.5	0	0	0	6.5
BaO	0.5	1.0	2.5	0	1.0	2.0	0	0	0	15.0
その他	2.0	2.5	1.5	3.5	1.0	2.0	0	1.0	0	0

The density and the strain point of said glass substrate were measured. Density measured about 20-g lump by the Archimedes method. The strain point was measured by the fiber enlargement method (JIS R3103-2). The result is shown in Table 2. [0041]

Subsequently, said glass substrate was immersed in 500 \*\* about Examples 1-6 and Examples 9 and 10 for 5 hours into the potassium nitrate fused salt which carried out heating maintenance, chemical strengthening treatment was performed, and the chemically-strengthened-glass board was obtained. About Examples 7 and 8, it was immersed in 450 \*\* for 5 hours into the potassium nitrate fused salt which carried out heating maintenance, chemical strengthening treatment was performed, and the chemically-strengthened-glass board was obtained. Next, the chemically-strengthened-glass board was fed into the belt furnace, with the ordinary pressure CVD method, a tin tetrachloride, water, methanol, and hydrogen fluoride were sprayed, the tin-oxide film was formed on the chemistry glass reinforced substrate, and the chemically-strengthened-glass board with a tin-oxide film was obtained in the membrane formation zone heated at 530 \*\*.

In Examples 1-10, sheet resistance values and the highest transmissivity in visible light were measured about the obtained chemically-strengthened-glass board with a tin-oxide film. Sheet resistance values were measured using the four point probe method by RORESUTA MCP-T250 (made by Mitsubishi Chemical). The highest transmissivity in visible light was measured on the conditions which do not have a rear-face coat using spectrophotometer UV1600 (made by Shimadzu).

As a result, the highest transmissivity in the visible light of the chemically-strengthened-glass board with a tin-oxide film in Examples 1-10 is not less than 90% in Examples 1-10. Sheet resistance values are 800-1200ohm/\*\*, and it checked that performance sufficient as a lower electrode of a touch panel was obtained.

## [0044]

Subsequently, the ratio of the surface pressure shrinkage stress which measured the depth of surface pressure shrinkage stress and a compressive stress layer, and was beforehand measured before membrane formation about the chemically-strengthened-glass board with a tin-oxide film in Examples 1-10, and the surface pressure shrinkage stress after membrane formation (surface pressure shrinkage stress before the surface pressure shrinkage stress / membrane formation after membrane formation.) Hereafter, it is called a compression stress ratio. It asked. Measurement of the depth of surface pressure shrinkage stress and a compressive stress layer was performed in surface stress meter FSM-60-V (made in the Orihara factory) using some cut-down flakes. The result is shown in Table 2.

The fracture strength of the chemically-strengthened-glass board with a tin-oxide film of acquired Examples 1-10 was measured with the concentric circle bend test method. That is, the chemically-strengthened-glass board with a tin-oxide film has been arranged on a retaining ring 46 mm in diameter, and fracture strength when load was applied and it destroyed at the crosshead speed of 1 mm/min to the film surface side using a ring 19 mm in diameter was searched for. Fracture strength examined every ten chemically-strengthened-glass boards each with a tin-oxide film, and calculated average value. As for fracture strength, it is preferred practically that they are 350 or more MPa. The result is shown in Table 2. [0046]

[Table 2]

	例 1	例 2	例3	例4	例 5	例 6	例 7	例 8	例 9	例 10
歪点	590	570	580	550	590	570	510	480	570	630
(℃)										
密度	2.55	2.54	2.60	2.55	2.54	2.52	2.50	2.45	2.46	2.77
(g/cm <sup>3</sup> )										
表面圧縮応力	390	430	390	340	530	450	150	170	<b>1</b> 90	-
(MPa)										
圧縮応力層の	40	80	60	100	30	50	20	130	20	-
深さ(μm)										
圧縮応力比	0.98	0.96	0.95	0.94	0.99	0.98	0.71	0.55	0.96	-
破壊応力	470	520	490	500	430	480	290	320	180	160
(MPa)										

# [0047]

As shown in Table 2, since Examples 1-6 was [ the strain point of a glass substrate ] not less than 550 \*\*, even if a compression stress ratio is close to about 1 and it let the membrane formation process pass, the fall of surface pressure shrinkage stress did not take place, and stress was not eased. As a result, fracture strength also became high and it was shown that it is practically sufficient intensity. Since it was a range whose depth of a compressive stress layer is still more preferred, when the chemically-strengthened-glass board with a transparent conducting film of Examples 1-6 was cut in the wheel cutter, only the glass substrate before chemical strengthening has cut by one 1.2 to 1.5 times the wheel pressure of this satisfactorily to the wheel pressure which can usually be being cut.

On the other hand, since a strain point was 510 \*\*, Example 7 whose glass substrate is soda lime glass had the low compression stress ratio, when it let the membrane formation process pass, the fall of surface pressure shrinkage stress took place, and it was shown that stress is eased during membrane formation. As a result, fracture strength was also low. Although the compressive stress layer was quite deep, since the strain point of a glass substrate was 480 \*\*, like Example 7, the surface pressure shrinkage stress after membrane formation became low by stress relaxation, and the fracture strength of Example 8 was also low. When the chemically-strengthened-glass board with a transparent conducting film was cut in the wheel cutter, since the compressive stress layer is deep, it cuts, a line could not enter easily, and even if it increased wheel pressure, it was not able to cut well. Although Example 9 had the strain point of mother glass as high as 570 \*\*, since it was small, intensity with it was not obtained for K<sub>2</sub>O. [ a slow ion-exchange rate and ] [ sufficient ] Since Example 10 had small Na<sub>2</sub>O content, it was not formed, so that it could distinguish the compressive stress layer, even if it carried out chemical strengthening treatment of it, and was quite low. [ of fracture strength ]

[0049]

[Effect of the Invention]

Since the strain point of a glass substrate is not less than 550 \*\* and the chemically-strengthened-glass board with a transparent conducting film of this invention can maintain the surface pressure shrinkage stress which stress relaxation did not happen easily during membrane formation, and was obtained by chemical strengthening treatment, even if it makes thickness of a glass substrate thin, it has practically sufficient intensity. Therefore, the chemically-strengthened-glass board with a transparent conducting film of this invention is preferred as a component for touch panels. A productivity drive is expectable when a possibility that membranes can be conventionally formed at an elevated temperature increases. Forming temperature ranges, such as films other than a transparent conducting film, for example, an alkali barrier film, an antireflection film, and an insulator layer, also spread. Furthermore, high temperature processing also of chemical strengthening becomes possible in a similar manner.

[Brief Description of the Drawings]

[Drawing 1] The figure explaining the composition of a touch panel

[Explanations of letters or numerals]

- 1: Film
- 2: The conducting film for films
- 3: Upper electrode
- 4: Transparent conducting film
- 5: Glass substrate
- 6: Lower electrode
- 7: Dot spacer
- 8: Input pen

[Translation done.]